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(54) System for the passivation of metal surfaces affected by operating conditions and agents promoting corrosion.

(57) System for the passivation of metal surfaces and more especially those in stainless steel, titanium, etc., in equipment used for chemical processes, where elements and compounds are formed which have a corrosive action more particularly where temperature and pressure are higher than ambient conditions, in which system the main passivating agent is oxygen (air) combined with at least a second auxiliary agent, characterized by the fact that the latter is ozone (O₃).

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This invention concerns a system for the passivation of metal surfaces in equipment affected by operating conditions and by agents which promote corrosion, in general of the surfaces in chemical plants involving the presence and formation of corrosive compounds especially where the environmental conditions (temperature and pressure) intensify said corrosive action.

5 More particularly the invention concerns a system for the passivation of the metal equipment used in chemical plants, and exposed to the intensive action of highly corrosive compounds, and what is more under temperature and pressure conditions higher than ambient conditions.

In an embodiment of great industrial interest, the invention consists in a system for the passivation of metal equipment used in urea synthesis and treatment processes.

10 Without affecting the generality of the invention, but only as a reference to one of the most interesting and immediate instances, in plants for the industrial production of urea through the synthesis of the reactants NH_3 and CO_2 , with the formation of various compounds, besides urea, which are highly corrosive such as more or less concentrated aqueous solutions of ammonium carbamate, ammonium carbonate, urea itself and other kinds of ionic species.

15 The metal surfaces of the various parts of equipment which come into contact with the above-mentioned compounds are subjected to chemical aggression which affects their integrity and efficiency.

It is well known that the synthesis of urea is carried out at a high temperature (on average $180+215^\circ\text{C}$) and high pressure (on average 130+400 bar). Downstream the synthesis section are found a number of decomposition stages of urea synthesis by-products which have not been transformed into urea such as
20 ammonium carbamate which through heat is decomposed into NH_3 and CO_2 and separated from the synthesis elements, as gaseous NH_3 and CO_2 , which are condensed in successive condensation stages forming aqueous solutions of ammonium carbamate and/or ammonium carbonate which are recycled in the synthesis section, while the urea is concentrated in successive stages operating at decreasing pressure until the final vacuum concentration stage is reached from which is obtained virtually pure melted urea
25 which is then sent to the finishing stage effected with various techniques.

Various systems have been put forward for the passivation of equipment used in the stages mentioned above which is subjected to aggression by the corrosive compounds treated in it. For example Belgian Patent No. 625.397 describes the use of oxygen as passivating agent at 180°C and 270 kg/cm² for the surfaces in a urea synthesis reactor in stainless steel containing up to 19% Cr and 14% Ni; in general
30 oxygen is replaced by other passivating agents, for example hydrogen peroxide and alkaline metal peroxide or alkaline earth peroxide. In European Patent 0096151 a passivation system is described for strippers where the effluent from the urea synthesis reactor is treated at a high temperature and pressure, between 120 and 240 kg/cm², as a thin falling film countercurrent with NH_3 or CO_2 ; to a first passivating agent consisting of oxygen-containing gas introduced from the bottom of at least one stripper is added as second
35 passivating agent a liquid injected from the top of the stripper and selected from hydrogen peroxide, alkaline metals persulphate or perborate, peracetic acid, organic peroxide.

Oxygen may be introduced into the plant as pure oxygen or mixed with air or with hydrogen peroxide.

The oxygen in gas form is introduced by injecting it into the CO_2 before this is compressed, or into the ammonia entering the synthesis zone, or as hydrogen peroxide into the various liquid flows upstream the
40 entrance to the equipment to be protected.

The passivating system with hydrogen peroxide requires in any case the simultaneous injection of gaseous oxygen, either as air or as pure oxygen as mentioned before.

The above-mentioned passivation systems are used to protect from corrosion the metal material usually employed in industrial plants for the production of urea (various types of stainless steel, titanium, etc.).

45 Besides the above-mentioned passivating agents others have been put forward (for example DE-A-1800755) such as soluble ammonium nitrite, soluble sodium nitrite, and other substances not used industrially.

Nowadays the technique universally adopted to passivate metal surfaces in contact with the solutions and vapours present in the plant's various stages is to send to the synthesis reactor air and oxygen by
50 injecting them into the CO_2 ; in some cases, besides this injection, hydrogen peroxide is introduced into the liquid flow upstream of the equipment to be passivated.

The oxygen content injected into the CO_2 has a concentration of between 0.2% and 0.8% in volume and this causes some troubles of which just a few pointed out as follows:

- 55 1. the oxygen injected as air enriches the reactor with nitrogen, with the obvious consequence that the synthesis zone is enriched with inerts, thus creating a gas phase the consequence of which is a reduction in urea yield in the reactor;
2. since the CO_2 comes from the synthesis gas decarbonation section for the production of ammonia, it contains H_2 , N_2 , CO , CH_4 in such proportions that together with the oxygen they create explosive

mixtures.

It has been seen that to escape the explosion field the amount of oxygen injected into CO₂ must be below 0.2% vol., but under these conditions it has also been observed that the protective action over the metal surfaces is greatly reduced thus leaving them exposed to the corrosive action of both liquid and gas substances present in the various parts of equipment.

Object of the present invention is now a process which eliminates the drawbacks of the present State of the Art and allows to overcome the situation of contrast between the necessity of having oxygen in large amount suitable for the desired passivation on one side and the necessity of avoiding the risks of explosion on the other side.

Surprisingly it has been found that to escape the field of explosion, the oxygen content may be reduced below 0.3% vol. without affecting the passivation of equipment, by means of adding to the passivation air small amounts of ozone (O₃).

The synergic action of the oxydization of air and O₃ permits the achievement of, among others, the following advantages:

3. notable reduction of inerts in the urea synthesis reactor with the advantage of an increase in urea yield.

4. reduction of the vapour phase in the reactor thus increasing the volume of the liquid phase increasing its residence time.

5. avoidance of the field of explosion, since the O₂ does not create an explosive mixture with the H₂, CO, CH₄ present in the various stages of the plant.

The advantage of the invention is undeniable and significant all the more since the production of O₃ is achieved with amply experimented conventional methods, just as absolutely conventional is the system for eliminating O₃ from the gas inerts discharged into the atmosphere where the laws for the protection of the environment forbid its being released into the atmosphere, the production of O₃ and its elimination being a well-known technique.

The content of O₂ in the CO₂ may vary between 0.05% vol. and 0.3% vol. while the content of O₃ may vary between 0.01% vol. and 0.1% vol. When a compound selected from the group consisting of hydrogen peroxide (H₂O₂), alkaline metals peroxides, alkaline earths peroxides, alkaline metals persulphates or perborates, organic peroxides and acetic acid is present together with O₂ and O₃, the oxygen amount can be reduced below 0.05% vol., i.e. between 0.01% vol. and 0.05% vol., preferably the third compound selected from the above group is hydrogen peroxide (H₂O₂).

A further advantage of the invention is that the concentration of O₃ may be maintained at a high level without the danger of explosions and with an appreciable increase in passivation, reducing the hydrogen (H₂) content (together with the CO, N₂ and CH₄ content) in the CO₂ obtained from the decarbonation plant of the ammonia synthesis gas, by preference through an additional pre-flash of the solution rich in CO₂ to be regenerated, before in effect it enters this regeneration stage.

The above pre-flash may be simply carried out at about 3 bar abs.

EXAMPLES

The purpose of the following examples is to compare the composition of the CO₂ sent to the synthesis reactor and of the inert gas discharged into the atmosphere, both according to the known technique and to the invention.

We take into consideration the case of a 1000 t/d urea plant:

Composition of the CO₂

Comparison example 1.

Known technique

The amount of CO₂ necessary for synthesis and its composition after the addition of air is as follows:

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	CO2	15610 Nm3/h	94.93 % vol.
	N2	491 "	2.98 "
5	H2	164 "	1.00 "
	O2	98 "	0.60 "
10	CO	traces "	traces "
	CH4	80 "	0.49 "

15	Total	16443 Nm3/h	100.00 % vol.

20 Example 2. Invention

The amount of CO2 necessary for synthesis and its composition after the addition of air enriched with O3 is as follows:

25	CO2	15610 Nm3/h	96.77 % vol.
	N2	245 "	1.52 "
	H2	164 "	1.02 "
30	O2	29 "	0.18 "
	O3	3 "	0.02 "
35	CO	traces "	traces "
	CH4	80 "	0.49 "

40	Total	16131 Nm3/h	100.00 % vol.

45 It can be seen that the amount of oxygen is appreciably reduced in the case of the invention as compared to the amount required for the known technique while the passivating effect is equally efficient thanks to the addition of ozone (O3).

Composition of the inert gas discharged into the air in the two cases:

50 Example 3

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	Known technique				Invention			
5	N2	491 Nm3/h	58.9 % vol.		245 Nm3/h	47.0 % vol.		
	H2	164 "	19.7 "		164 "	31.5 "		
	O2	98 "	11.8 "		29 "	5.5 "		
10	O3	-	-		3 "	0.6 "		
	CO	traces	-		traces	-		
15	CH4	80 "	9.6 "		80 "	15.4 "		
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		833 Nm3/h	100.0 % vol.		521 Nm3/h	100.0 % vol.		

The field of explosion of the two mixtures can easily be calculated by conventional method and it will be seen that the mixture in example 3 according to the invention is outside the limits of explosion.

The invention has been deliberately described and exemplified with reference to urea which is one of the most difficult cases and quite emblematic as far as the phenomenon of corrosion is concerned. Of course the invention can be applied to the majority of analogous cases, and more particularly to all chemical processes where, as for urea, it is necessary to passivate with oxygen (air) with or without a peroxide; now, according to the invention, passivation is synergically improved with the addition of O3. Application to these processes remains therefore within the scope and the spirit of this invention.

Claims

1. System for the passivation of metal surfaces and more especially those in stainless steel, titanium, etc., in equipment used for chemical processes, where elements and compounds are formed which have a corrosive action more particularly where temperature and pressure are higher than ambient conditions, in which system the main passivating agent is oxygen (air) combined with at least a second auxiliary agent, characterized by the fact that the latter is ozone (O3).
2. System according to claim 1, characterized by the fact that the O3 is obtained from air or from oxygen.
3. System according to claim 1 or 2, characterized by the fact that the amount of O3 added to the oxygen is between 0.01% and 0.1% in volume on the volume of O2, the latter being by preference smaller than 0.2% in volume.
4. System according to claim 3, characterized by the fact that a compound selected from the group consisting of hydrogen peroxide (H2O2), alkaline metals peroxides, alkaline earths peroxides, alkaline metals persulfates or perborates, organic peroxides and acetic acid, is present together with oxygen (O2) and ozone (O3).
5. System according to one of claim 1, 2, 3 or 4, used in particular for the passivation of equipment for the synthesis of urea from NH3 and CO2 and for the treatment of the compounds which accompany it, and more particularly for urea synthesis reaction and concentration equipment, for ammonium carbamate decomposition and condensation equipment, etc. etc., in Cr, Ni, etc. etc., stainless steel, in titanium etc. etc., characterized by the fact that air additioned with O3 is injected into the feed and/or recycle of CO2 and/or NH3 flow and/or into further liquid and/or gas flows.
6. System according to claim 5, characterized by the fact that the oxidizer O3 present in the CO2 may vary in volume between 0.001% and 0.3%.

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7. System according to claim 6, in which the oxidizer O₃ present in the CO₂ varies between 0.01% and 0.2% in volume by preference between 0.1% and 0.18% in volume when the CO₂ has a low hydrogen content, having been obtained from the CO₂ absorption section with its own pre-flash in order to remove hydrogen, together with CO and nitrogen from the solution which has absorbed the CO₂ before entering the regeneration column.
8. System according to claim 5, characterized by the fact that the concentration of the oxidizer O₃ in the liquid flows may vary between 2 and 1000 ppm.



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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 3043

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	FR-A-1 027 202 (MAX STROTZEL) * page 1, column 1, line 33 - line 41 * * page 1, column 2, line 1 - line 13; claims A, B1, 2 *	1,5	C23C8/12 C23C8/14 C07C273/04
Y,D	EP-A-0 096 151 (MONTEDISON) * claim 1 *	1,5	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C23C C07C
A	* claim 1 *	4	
A	wpil/derwent, abstract nr. 85-187612 c31, derwent publications, london, gb & jp-a-60116760 (HITACHI)24-06-85 *abstract*	1-3	
A	derwent publications, london, gb, nr.40982c/23 week c23 16-07-80 & su-a-446181(lengd elec eng inst) 15-10-79 *ABSTRACT*	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 JUNE 1992	Examiner ELSEN D, B.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			

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